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EPOXIDES AS ACTIVATORS FOR GRAFTING OF POLY(TETRAHYDROFURAN) FROM POLY(METHYLPHENYLSILYLENE)

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Abstract:

Epoxides have been found as efficient activators for initiation of the cationic polymerization of tetrahydrofuran by trimethylsilyl trifluoromethanesulfonate. They can also activate partially triflate polysilane and lead to grafting of the polyTHF from polysilanes.

Introduction

Polysilanes consist of a Si-Si sigma conjugated backbone. Strong electron delocalization along the backbone results in interesting photochemical properties which lead to potential applications in electronics, optics, and ceramics. Polysilanes are typically prepared by the reductive coupling of dichlorosilanes with sodium in refluxing toluene.[1,2] We have prepared monomodal high molecular weight poly(methylphenylsilylene) (PSI) by using ultrasound at ambient temperatures.[3] Because of the severe reaction conditions involved with the reductive coupling the selection of dichlorosilanes is limited to alkyl and aryl substituents.

Recently, we discovered that the phenyl groups of PSI can be displaced by using trifluoromethanesulfonic (triflic) acid (HOTf).[4] The resulting electrophilic silyl triflate moieties are capable of reacting with a variety of nucleophiles. We have taken advantage of this reactivity and utilized these sites to initiate the cationic ring opening polymerization of tetrahydrofuran (THF). The target comb-like graft copolymers may exhibit new and interesting morphologies as a result of phase separation of the two polymers.

Experimental

All experiments were run in a dry box under inert atmosphere (model HE-493, Vacuum Atmospheres Co.). PSI was prepared as described previously.[3] Methylene chloride was triple distilled and stored over calcium hydride under nitrogen. HOTf was distilled on a high vacuum line and stored in an ampule in the dry box. 2,6-Di-*tert*-butylpyridine and methanol were used as received. THF was distilled from sodium/benzophenone and stored over sodium-potassium alloy. 1,2-Propylene oxide was distilled from calcium hydride. GPC data was obtained using a Waters 510 HPLC pump equipped with a Waters 712 WISP autosampler, Waters 991 photodiode array detector and a Waters 410 differential refractometer. The columns used were Phenomenex phenogel linear, 10^3Å, and 10^2Å arranged in series. Calibration was based on polystyrene standards (Shodex) and the solvent used was THF. NMR data was obtained from an IBM NR/300 300 MHz FT NMR Spectrometer.

Results and Discussion

Model Studies

Trimethylsilyl trifluoromethanesulfonate (TMSOTf) has been reported as a useful initiator for the cationic polymerization of heterocyclics and alkenes.[5] We have discovered, however, that TMSOTf alone is not an efficient initiator for the cationic ring opening polymerization of THF.[6] When TMSOTf reacts with a THF molecule, the positive charge in the resulting trimethylsilyl-tetrahydrofuranium cation is mostly distributed onto the exocyclic trimethylsilyl group. Attack by subsequent THF molecules at the α-endocyclic carbon atom that would lead to ring opening is preceded by attack at the trimethylsilyl group resulting in a reversible exchange reaction. Eventually, ring opening takes place, but the initiation reaction is so slow the polymers produced have higher than expected molecular weights and broader molecular weight distributions.

To overcome these problems, we have employed the use of promoters to create a faster, more efficient initiation process. Promoters react quickly with TMSOTf to create a highly reactive species that can be attacked by THF. The resulting tetrahydrofuranium cation contains an exocyclic alkyl group instead of a trimethylsilyl group so the charge distribution favors ring opening. We have studied acetone, 1,3-dioxolane, and 1,2-propylene oxide (PRO-OX) as promoters and found PRO-OX to be the most successful.[7]

Recent studies have indicated that a 10:1 ratio of PRO-OX:TMSOTf produces the best results. The number average molecular weights of the resulting polymers are close to the theoretical M_n (assuming each TMSOTf molecule initiates the growth of one polyTHF chain). The polydispersities are more narrow than when other PRO-OX:TMSOTf ratios are used. These results are presented in Table 1.

Grafting from Low Molecular Weight PSI

Having found an optimal PRO-OX:TMSOTf ratio, we then proceeded on to the grafting of THF from partially triflated low molecular weight PSI in the presence of PRO-OX. Low molecular weight PSI (M_n=4329, DP=36) was reacted with HOTf in order to displace 20% of the phenyl groups. This should produce an average of 7.2 triflate moieties per PSI chain. After allowing sufficient time for this reaction to take place, 2,6-di-*tert*-butylpyridine (PYR) was added to the reaction mixture to quench any remaining HOTf. PYR is a very efficient and selective proton trap.[8] It does not react with silyl triflates or

growing tetrahydrofuranium cations. This is important, because free HOTf can initiate the polymerization of THF leading to homo-polyTHF impurities. Fourteen hours after the addition of PRO-OX and THF, the solution was very viscous and the reaction was terminated with methanol and PYR. The resulting graft copolymer was precipitated from excess methanol and analyzed by GPC and ^{1}H NMR. Table 2 contains molecular weight data for the polymers involved in the grafting process There is a small high molecular weight shoulder in the original PSI. The Mn of the triflated PSI is smaller than that for the original PSI and the polydispersity is more narrow. This is due to a small extent of cleavage of Si-Si bonds in the PSI backbone by HOTf. This type of cleavage is more noticeable with high molecular weight PSI, because a greater change in molecular weight will result then when low molecular weight PSI is partially degraded. Molecular weight of the graft copolymer is much higher. The Mn value of 47,940 is less than the expected theoretical value of approximately 64,000. This may be due to inefficient polymerization at the later stages due to the high viscosity of the solution. The polydispersity of the graft copolymer is 3.28.

The GPC analysis employs the use of two detectors; a photo-diode array detector (UV) and a differential refractive index detector (RI). The RI response of PSI is extremely weak compared to the UV response. In addition, polyTHF has no UV response. As a result, the presence of a strong RI reponse that corresponds to the UV reponse is a very good indicator that polyTHF is indeed grafted onto PSI. We also employed the photo-instability of PSI to help confirm the quality of the graft copolymer. PSI can be degraded by strong UV light, whereas polyTHF cannot. The graft product (in THF) was exposed to UV light and re-analyzed by GPC. No UV response was detected after exposure. A RI response was seen at a molecular weight lower than the graft copolymer, since the polyTHF chains are no longer held together by the PSI backbone. The Mn of the free polyTHF was 10,610, which is higher than the expected theoretical value of 8300. This indicates that the concentration of grafting sites was lower than expected. This may be due to incomplete triflation, inefficient activation, or some side reactions. The polydispersity was 2.14, not unexpected from a reversible polymerization system such as THF.

The graft copolymer was also analyzed by ^{1}H NMR. Large peaks were detected for polyTHF at 3.40 ppm ($-CH_2-O-CH_2-$) and 1.60 ppm ($-CH_2-CH_2-$). The peaks for PSI were very small, since PSI only composes a small percentage of the copolymer. These broad peaks were seen in the ranges of 6.6-7.2 ppm (Si-

phenyl) and -1-0 ppm (Si-CH3). The molecular weight distribution in this system is broader than the low molecular weight PSI system due to the larger changes in molecular weight caused from Si-Si cleavage by HOTf. The PSI peaks are easier to see in the NMR spectrum, however, because the percent composition of PSI is greater than in the low molecular weight PSI graft copolymer. In addition to the polyTHF peaks and PSI peaks, a small doublet is present at 1.10 ppm, and a small singlet is at 0 ppm. The doublet can be attributed to the methyl group of the PRO-OX units incorporated in the polymer chain during initiation. The origin of the singlet is not completely understood at this time.

All of the above results indicate that poly(methylphenylsilylene)-g-poly(tetrahydrofuran) has been prepared by cationically polymerizing THF from active silyl triflate moieties on low molecular weight poly(methylphenylsilylene) in the presence of 1,2-propylene oxide. These copolymers may exhibit interesting morphologies due to phase separation and will be studied by electron microscopy. Future studies will also involve the grafting of 2-methyl-2-oxazoline (MeOXZ) from triflated PSI in the presence of PRO-OX. Model studies using TMSOTf to initiate the polymerization of MeOXZ showed that an unusual mode of ring opening took place, resulting in the formation of a stable dimeric cation.[9] As in the THF system, the use of PRO-OX as a promoter overcomes these problems leading to fast, efficient initiation.

Table 1
Molecular Weights and Polydispersities for PolyTHF

[THF]$_0$	[TMSOTf]$_0$	[PRO-OX]$_0$	Mn	Mw/Mn
8.1	0.03	0.03	21,695	1.99
7.9	0.08	0.32	7,006	1.75
7.9	0.08	0.80	5374	1.65

Table 2
Molecular Weights and Polydispersities for Grafting Reaction

Sample	Mw	Mn	Mw/Mn
Original PSI	17,856	4,329	4.12
Triflated PSI	7,318	3,271	2.24
PSI-gpolyTHF	157,401	47,940	3.28
PolyTHF*	22,691	10,610	2.14

*After copolymer degradation by UV light

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